

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-067994

(43)Date of publication of application : 10.03.1998

(51)Int.Cl.

C10L 3/10

C01B 31/20

C10J 3/46

C10J 3/72

(21)Application number : 08-226543

(71)Applicant : MITSUBISHI HEAVY IND LTD

(22)Date of filing : 28.08.1996

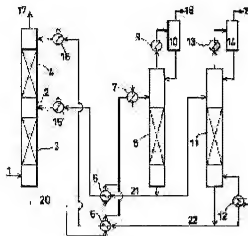
(72)Inventor : IJIMA MASAKI
MITSUOKA SHIGEAKI
TANAKA YUJI

(54) **ADVANCED REMOVAL OF CARBON DIOXIDE IN HIGH-PRESSURE RAW MATERIAL GAS, HIGH-PRESSURE RECOVERY AND APPARATUS THEREFOR**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for removing carbon dioxide in a high-pressure raw material gas by which the carbon dioxide at a high concentration in a natural gas or various gases under a high pressure is removed to a trace concentration with a carbon dioxide absorbent and the carbon dioxide is then recovered from the absorbent under a high pressure.

SOLUTION: A raw material gas 1 containing carbon dioxide is fed to a decarbonator column 2 and brought into contact with a liquid of a partial regenerating absorbent 21 in a lower absorbing section 3 to partially absorb the carbon dioxide. The resultant gas is then brought into contact with a liquid of a regenerating absorbent 22 in an upper absorbing section 4 to absorb the carbon dioxide until a minor concentration thereof attains. The carbon dioxide is further recovered



from the regenerating absorbent 22 under a high pressure.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention the high-concentration carbon dioxide (CO_2) in high-pressure natural gas or various synthesis gas, It removes to minute amount concentration using a carbon dioxide lean solution, the purified gas whose carbon dioxide levels are 10-10000 ppm is obtained, and it is further related with the method of collecting carbon dioxide from this lean solution with high voltage, and its device.

[0002]

[Description of the Prior Art]The considerable amount, for example, 10 to 20% of carbon dioxide, may usually be contained in high-pressure natural gas. Since carbon dioxide serves as dry ice and produces problems, such as a blockade of a device, as a solid with cooling in making such natural gas into liquefied natural gas (henceforth LNG), it is necessary to reduce the concentration of carbon dioxide to 50 ppm or less.

[0003]In the example of ammoniuria matter composition, partial oxidation of natural gas, the naphtha, etc. is carried out, or it reforms using a steam, and mixed gas, such as hydrogen, carbon monoxide, and carbon dioxide, is obtained. After performing CO water gas shift reaction for this further and converting carbon monoxide into carbon dioxide, carbon dioxide is separated and it is considered as an ammonia synthesis raw material. On the other hand, the separated carbon dioxide is pressurized by 100-200 atmospheres, reacts to ammonia, and generates urea. For this reason, generally it is necessary to reduce the concentration of the carbon dioxide in an ammonia synthesis raw material to about 500 ppm.

[0004]It is necessary to remove carbon dioxide to the grade of tens - 1000 ppm of numbers in the example of synthetic service-water matter gas according to those uses. The separated carbon dioxide needs to pressurize tens of atmospheres - hundreds of atmospheres, in order to dispose to subterranean aquifer as the 3rd recovery (EOR) of a crude oil, a liquefied carbon dioxide and said urea composition, and a battle against global warming. For this reason, when the carbon dioxide which removed a small amount of carbon dioxide until it reached concentration, and was removed from high-pressure material gas from the first could be collected in the high-pressure state, it was desirable, but the method for it was not known.

[0005]In the Prior art, in order to remove a small amount of carbon dioxide, for example to about 100 ppm to concentration, the following methods are adopted. First, supply gas to a decarbonator pars basilaris ossis occipitalis, supply a carbon dioxide lean solution from a decarbonator crowning, this lean solution is made to absorb carbon dioxide by gas-liquid contact, and it removes. Subsequently, it is made the lean solution (henceforth a reproduction lean solution) which carried out steam stripping of the liquid (henceforth a load lean solution) which absorbed this carbon dioxide in the regeneration tower, and removed carbon dioxide, and the method of supplying this reproduction lean solution to decarbonator is known. Methods of removing carbon dioxide from high-pressure natural gas, and collecting the removed carbon dioxide in the high-pressure state include the method of carrying out bulk removal of the carbon dioxide.

[0006]

[Problem(s) to be Solved by the Invention]However, there were the following problems in advanced removal and the high voltage recovery method of the above-mentioned conventional carbon dioxide, and its device.

(1) In the method using the above-mentioned carbon dioxide lean solution, since the carbon dioxide levels in a reproduction lean solution can be reduced, a small amount of carbon dioxide is removable to concentration, but. In order to carry out depressuring and to reproduce, it is difficult to collect carbon dioxide by sufficient pressure, and it needed to pressurize by the compressor again.

(2) In the method of the above-mentioned bulk removal, 1% - about 5% of carbon dioxide remained in natural gas after being removed. In light of the above-mentioned circumstances, this invention provides the method of removing high-pressure natural gas or the high concentration carbon dioxide in various synthesis gas to minute amount concentration using a carbon dioxide absorbent, and collecting carbon dioxide from this absorbent with high voltage.

[0007]

[Means for Solving the Problem]This invention persons absorb carbon dioxide in material gas by a lean solution, as a result of inquiring wholeheartedly, Separate carbon dioxide for this carbon dioxide load lean solution by a high pressure state with heating, carry out partial regeneration of the lean solution, and carry out the cyclic use of waste water by making that part into a partial regeneration lean solution, and. By reproducing highly and carrying out the cyclic use of waste water of a part of partial regeneration lean solution, it finds out that carbon dioxide is recoverable by a high pressure state at the same time carbon dioxide in material gas is highly removable, and it came to complete this invention.

[0008]Namely, high-pressure material gas more than pressure 2 kg/cm^2 (absolute pressure) which contains carbon dioxide 2 to 50% according to this invention, Supply decarbonator which consists of a lower absorption part and a top absorption part, gas-liquid-contact-carry out partial absorption of the carbon dioxide by making material gas into a partial regeneration lean solution by a lower absorption part, carry out gas-liquid contact to a reproduction lean solution by a top absorption part, and a small amount of carbon dioxide is absorbed and removed to concentration, Obtain purified gas whose carbon dioxide levels are 10-10000 ppm, and discharge out of a system, and. Supply a carbon dioxide load lean solution produced in decarbonator to a high voltage regeneration tower, and a carbon dioxide load lean solution is heated, After emitting some carbon dioxide under 2 kg/cm^2 (absolute pressure) - application of pressure of a feed gas pressure and obtaining a partial regeneration lean solution, Supply a part of partial regeneration lean solution to a lower absorption part, supply the remainder to a low-pressure regeneration tower, make carbon dioxide emit and obtain a reproduction lean solution, and supply a reproduction lean solution to a top absorption part, carry out vapor liquid separation from moisture which cools carbon dioxide emitted under application of pressure in a high voltage regeneration tower, and is accompanied, and it collects carbon dioxide under application of pressure, Advanced removal and a high voltage recovery method of carbon dioxide in high voltage material gas characterized by here vapor liquid separation is carried out here from moisture which cools carbon dioxide emitted in a low-pressure regeneration tower, and is accompanied, and collects carbon dioxide, and its

device are provided.

[0009]

[Embodiment of the Invention]The material gas used as the object processed by this invention is high voltage, and is the natural gas and the various synthesis gas containing carbon dioxide. For example, it is gas containing the carbon dioxide after being obtained from naphtha, natural gas, a fuel oil, corks, etc. by steam reforming or partial oxidation, performing CO water gas shift reaction and converting carbon monoxide into carbon dioxide. It is gas after desulfurization treatment is carried out and sulfur compounds decrease in number to 100 ppm or less preferably. Although there is no restriction in particular in the pressure of material gas, more than 2 kg/cm^2 is preferred. It is more than 10 kg/cm^2 still more preferably. Although there is no restriction in particular also about the maximum of a pressure, it is usually $200\text{-}300 \text{ kg/cm}^2$. And although there is no restriction in particular in the carbon dioxide levels in material gas, 1% - 50% are preferred. It is 10 to 30% still more preferably.

[0010]Purified gas after processing by this invention is the almost same pressure as material gas, and 1-10000 ppm of carbon dioxide levels are 10-1000 ppm preferably. As for the carbon dioxide lean solution used by this invention, the solution of various basic compounds or those mixtures is used. What has the following absorption performances in selection of a lean solution is preferred. That is, after a carbon dioxide lean solution carries out gas-liquid contact to material gas and absorbs carbon dioxide, it separates some carbon dioxide in a high voltage regeneration tower, partial regeneration is carried out, and the cyclic use of waste water is carried out to a lower absorption process. However, when the partial pressure of carbon dioxide is more than 2 kg/cm^2 as absorption performance, It is required for the difference of the saturation absorbed amount of the carbon dioxide at absorption temperature (for example, 40°C) and partial regeneration temperature (for example, 120°C) to be beyond constant value (for example, more than a $30\text{-Nm}^3\text{CO}_2/\text{m}^3$ lean solution), It is more than a $40\text{-Nm}^3\text{CO}_2/\text{m}^3$ lean solution preferably.

[0011]Usually, if temperature and the partial pressure of carbon dioxide are specified as for the above-mentioned lean solution, according to the absorption saturation curve of carbon dioxide to the lean solution, a saturation absorbed amount will serve as a specific value, without hardly being influenced by the kind of carbon dioxide gaseous mixture. In this invention, carbon dioxide is separated with heating, without carrying out depressuring of the load lean solution obtained from the high-pressure natural gas more than pressure 30 kg/cm^2 by absorbing and removing carbon dioxide using a partial regeneration lean solution in a partial regeneration process, as shown in the example mentioned later. Therefore, at an absorption process, carbon dioxide can be easily absorbed under low temperature and a low partial pressure, and the lean solution which carbon dioxide tends to separate under an elevated temperature and high partial pressure is used as a desirable lean solution in a regeneration process.

[0012]Therefore, the above-mentioned carbon dioxide lean solution is preferred, and physical absorption liquid or the lean solution of the base of physical absorption nature is used. It is amines, amino acid, and those alkali metal salt, and, specifically, the strong amines of chemical absorption nature, alkali metal carbonate, etc. can be added as occasion demands. Hindered amine etc. are mentioned as a base of the above-mentioned physical absorption nature. As hindered amine, N-methyldiethanolamine (MDEA),

triethanolamine (TEA), dimethylamino 1,3-propanediol (DMAPD), diethylamino 1,3-propanediol (DEAPD), etc. are mentioned.

[0013]Potassium carbonate is mentioned as alkali metal salt. In the above-mentioned basic compound, carbon dioxide absorption enhancers, such as a piperazine, a substitution piperazine, piperidine, and substituted piperidine, can be added. These absorbents are used as 20 to 80% of solution, although based on the kind of absorbent, and a service condition. The carbon dioxide lean solution can also add solvents, such as N-methyl pyrrolidone and sulfolane, as occasion demands. Although the high-pressure carbon dioxide collected from a carbon dioxide lean solution is based on the use of material gas and carbon dioxide, the pressure of more than 2 kg/cm^2 is desirable 10 kg/cm^2 - the almost same pressure grade as material gas.

[0014]Therefore, the cooking temperature of a load lean solution is $90\text{--}150^\circ\text{C}$, preferably, it is $100\text{--}140^\circ\text{C}$, partial discharge of the moisture from a load lean solution and carbon dioxide is performed [a high voltage regeneration tower is operated by the above-mentioned pressure,], and partial regeneration of the load lean solution is carried out. In order to reproduce a partial regeneration lean solution still more highly, preferably, it is $110\text{--}140^\circ\text{C}$ conditions, and below operating pressure power 2 kg/cm^2 is carried [$0.5\text{--}1 \text{ kg/cm}^2\text{G}$ and $100\text{--}150^\circ\text{C}$ of solution temperature] out, carrying out heating circulation, for example with a reboiler. The grade of reproduction of the partial regeneration lean solution supplied to the lower absorption part of decarbonator, the grades of reproduction of the reproduction lean solution supplied to a top absorption part, and those rates of a delivery late, It is dependent on the kind of lean solution, the carbon dioxide levels of material gas, the carbon dioxide levels of conditions, such as a pressure, and purified gas and also the flow of the carbon dioxide collected with high voltage, concentration, a pressure, etc. For example, the grades of partial regeneration are $0.05\text{--}0.3\text{-mol CO}_2 / \text{mol lean solution}$, reproductive grades are $0.01\text{--}0.1\text{-mol CO}_2 / \text{mol lean-solution grade}$, and the ratio supplied to the decarbonator of a partial regeneration lean solution is 30 to 95%.

[0015]Hereafter, the method of this invention is explained concretely, referring to drawing 1. The material gas 1 is supplied to the pars basilaris ossis occipitalis of the decarbonator 2, partial absorption is carried out, and carbon dioxide is further gas-liquid-contact-absorbed to concentration in very small quantities by the top absorption part 4 by carrying out gas-liquid contact to the partial regeneration lean solution 21 by the lower absorption part 3, and making carbon dioxide into the reproduction lean solution 22, and it is discharged out of a system as the purified gas 17. In the above, the lean solution 22 which flowed down while carrying out gas-liquid contact by the top absorption part 4 is mixed with the partial regeneration lean solution 21 by the lower absorption part 3, it flows down, carrying out gas-liquid contact, and is discharged from the pars basilaris ossis occipitalis of the decarbonator 2.

[0016]After the carbon dioxide load lean solution 20 which came out of the pars basilaris ossis occipitalis of the decarbonator 2 carries out heat exchange to the partial regeneration lean solution 21 or the reproduction lean solution 20 by the heat exchanger 5 or 6 and also is heated by predetermined temperature with the warmer 7, it is supplied to the high voltage regeneration tower 8 by necessity. The lean solution 21 by which partial regeneration was carried out is discharged from high voltage regeneration tower 8 pars basilaris ossis occipitalis, it is cooled by the heat exchanger 5, and if a part is required, it

is further cooled by the heat exchanger 15, and it is supplied to the lower absorption part 3. The moisture and carbon dioxide which were emitted from the crowning of the high voltage regeneration tower 8 are cooled by the capacitor 9, the gas liquid separation device 10 separates into water and the high-pressure carbon dioxide 18, and water flows back in the crowning of the high voltage regeneration tower 8, and by or necessity. A part is supplied to the crowning of the absorption tower 2, and may be used for the flowing-back water of recovery of a lean solution, or a low-pressure regeneration tower.

[0017]The remainder of the partial regeneration lean solution 21 being supplied to the low-pressure regeneration tower 11, being operated with less than 2 kg/cm^2 or decompression with absolute pressure, and heating a bottom with the reboiler 12, discharge of moisture and carbon dioxide is performed and a partial regeneration lean solution is reproduced highly. The grade of reproduction of a load lean solution is decided by the cooking temperature, holding time, and operating pressure power of the load lean solution in the low-pressure regeneration tower 11. The reproduced lean solution 22 is discharged from the pars basilaris ossis occipitalis of the low-pressure regeneration tower 11, it is cooled by the heat exchanger 6, and if a part is required, it is further cooled by the heat exchanger 16, and it is supplied to the top absorption part 4. [0018]The moisture and carbon dioxide which were emitted from the crowning of the low-pressure regeneration tower 11 are cooled by the capacitor 13, the gas liquid separation device 14 separates into water and the low-pressure carbon dioxide 19, and water flows back in the crowning of the low-pressure regeneration tower 11, and by or necessity. A part is supplied to the crowning of the absorption tower 2, and may be used for the flowing-back water of recovery of a lean solution, or a high voltage regeneration tower. As long as gas-liquid contact is efficient and an absorption tower and various regeneration towers have little pressure loss, they may be tray towers or may be packed columns. The packing can use various things, such as the conventional ** wall type.

[0019]Although much quantity of carbon dioxide recoverable with high voltage by this invention is so economical that there is, in the most desirable case, not less than 90% of carbon dioxide is preferably recoverable not less than 70% not less than at least 50%. Thus, since carbon dioxide is recovered by high voltage in this invention, compression power is saved substantially and can also reduce the scale of equipment.

[0020]

[Example]Hereafter, although an example explains this invention in detail, this invention is not limited to this.

(Example 1) The case where the carbon dioxide in the material gas for ammonia synthesis produced by reforming natural gas is removed by the method shown in process drawing of drawing 1 using the solution of 45wt%MDEA and a 4wt% piperazine as a lean solution is explained. The material gas containing hydrogen, nitrogen, hydrocarbon, and 19vol% of carbon dioxide was supplied to the lower part of the absorption tower under pressure 34 kg/cm^2 , the temperature of 45 **, and the conditions of flow $^3\text{ [of } 292,000\text{ Nm }]/\text{hr}$.

[0021]In the absorption tower, the material gas going up carried out gas-liquid contact to 1716 m of partial regeneration lean-solutions $^3/\text{hr}$ in the lower absorption part. As for material gas, in the lower absorption part, partial removal of the carbon dioxide levels was made even about 2 vol(s)%. In the top absorption part, gas-liquid contact of the material gas was carried out to 163 m of reproduction lean-solutions $^3/\text{hr}$, it turned into

refining material gas of carbon dioxide levels of 490 ppm, the temperature of 39 **, and pressure 33 kgG/cm², and was discharged from the absorption tower crowning. The load lean solutions which absorbed carbon dioxide are 55 ** of solution temperature. The carbon dioxide of the about 78-Nm³CO₂/m³ lean solution is included, and it was heated by 120 ** after heat exchange, and the high voltage regeneration tower was supplied and partial regeneration was carried out.

It was cooled by the capacitor and the separated carbon dioxide, water, and a little absorbents were separated by the gas liquid separation device from carbon dioxide. At about 40 **, the carbon dioxide by which cooling separation was carried out is pressure 10 kgG/cm², is flow ³[of 49,800 Nm]/hr, was compressed into 190 kgG/cm² by the compressor which is not illustrated, and was used for urea composition.

[0022]On the other hand, the partial regeneration lean solution extracted from the bottom of the high voltage regeneration tower is 100 **.

The carbon dioxide of the 43-Nm³CO₂/m³ lean solution is included, heat exchange was carried out to the load lean solution, it was cooled by 38 more **, and the lower absorption part of the absorption tower was supplied.

It was supplied to the low-pressure regeneration tower, remaining 163-m³/hr of the partial regeneration lean solution was decompressed by 0.85 kgG/cm², emitted carbon dioxide and water from the overhead, and was reproduced. The bottom was heated by about 110 ** with the reboiler formed in the low-pressure regeneration tower lower part, and was recycled by the low-pressure regeneration tower, and the reproduction lean solution containing the carbon dioxide of a 1.2-Nm³CO₂/m³ lean solution was obtained. It was cooled by the capacitor and the separated carbon dioxide, water, and a little absorbents were separated by the gas liquid separation device from carbon dioxide. At about 40 **, the carbon dioxide by which cooling separation was carried out was pressure 0.35 kgG/cm², and was flow ³[of 5,700 Nm]/hr.

[0023]The reproduction lean solution extracted from the bottom of a low-pressure regeneration tower is about 110 ** in temperature, and was supplied to the top absorption part of the absorption tower. In the meantime, a 110 ** reproduction lean solution carried out heat exchange to the low-temperature load lean solution, and was cooled to 38 more **. That by which the recovery amounts of carbon dioxide were collected from the high voltage regeneration tower is 90%.

It was 10% which was collected from the low-pressure regeneration tower. Thus, the carbon dioxide in ammonia synthesis material gas fell to sufficient concentration to supply an ammonia synthesis process, and since the pressure of the collected carbon dioxide was high, compression power required for urea composition was saved, and the scale was also reduced by equipment.

[0024](Example 2) The case where the process of drawing 1 removes the carbon dioxide in the material gas for ammonia synthesis produced by reforming natural gas using the solution of 45wt%MDEA and a 4wt% piperazine as a lean solution is explained. The material gas 1 containing hydrogen, nitrogen, hydrocarbon, and 19vol% of carbon dioxide was supplied to the lower part of the absorption tower 2 under pressure 34 kgG/cm², the temperature of 45 **, and the conditions of flow ³[of 292,000 Nm]/hr.

[0025]In the absorption tower 2, the material gas 1 going up carried out gas-liquid contact to the partial regeneration lean solution (1716-m³/hr) 21 in the lower absorption part 3. As for the material gas 1, in the lower absorption part 3, partial removal of the

carbon dioxide levels was made even about 2 vol(s)%. In the top absorption part 4, gas-liquid contact of the material gas 1 was carried out to the reproduction lean solution (200-m³/hr) 22, it became purified gas of carbon dioxide levels of 50 ppm, the temperature of 39 **, and pressure 33 kgG/cm², and was discharged from the absorption tower crowning. The load lean solution 20 which absorbed carbon dioxide contains the carbon dioxide of the about 78-Nm³CO₂/m³ lean solution, and was heated by 120 ** after heat exchange, it was supplied to the high voltage regeneration tower 8, and partial regeneration was carried out. It was cooled by the capacitor 9 and the separated carbon dioxide, water, and a little absorbents were separated by the gas liquid separation device 10 from the carbon dioxide 18. The carbon dioxide 18 by which cooling separation was carried out is the temperature of about 40 **, and pressure 33 kgG/cm², and is flow ³[of 49,640 Nm]/hr. It was compressed into 150 kgG/cm² by the compressor which is not illustrated, and was used for urea composition.

[0026]On the other hand, the partial regeneration lean solution 21 extracted from the bottom of the high voltage regeneration tower 8 is 100 ** in temperature. The carbon dioxide of the 29.2-Nm³CO₂/m³ lean solution is included, heat exchange was carried out to the load lean solution 20, it was cooled by 38 more **, and the lower absorption part 3 of the absorption tower 2 was supplied. It was supplied to the low-pressure regeneration tower 11, remaining 200-m³/hr of the partial regeneration lean solution 21 was decompressed by 0.85 kgG/cm², emitted carbon dioxide and water from the overhead, and was reproduced. The bottom was heated by about 110 ** with the reboiler 12 formed in the lower part of the low-pressure regeneration tower 11, and was recycled by the low-pressure regeneration tower 11, and the reproduction lean solution 22 containing the carbon dioxide of a 5-Nm³CO₂/m³ lean solution was obtained. It is cooled by the capacitor 13 and the separated carbon dioxide, water, and a little absorbents are separated by the gas liquid separation device 14 from the carbon dioxide 19. At about 40 **, the carbon dioxide 19 by which cooling separation was carried out was pressure 0.35 kgG/cm², and was flow ³[of 5,500 Nm]/hr. [0027]The reproduction lean solution 22 extracted from the bottom of the low-pressure regeneration tower 11 is about 110 ** in temperature, and is supplied to the top absorption part 4 of the absorption tower 2. In the meantime, the 110 ** reproduction lean solution 22 carried out heat exchange to the low-temperature load lean solution 20, and was cooled to 38 more **. That by which the recovery amounts of carbon dioxide were collected from the high voltage regeneration tower 8 is 90%.

It was 10% which was collected from the low-pressure regeneration tower 11. Thus, the carbon dioxide in ammonia synthesis material gas fell to sufficient concentration to supply an ammonia synthesis process, and since the pressure of the collected carbon dioxide was high, compression power required for urea composition was saved, and the scale of equipment was also reduced.

[0028](Example 3) The case where the carbon dioxide in natural gas is removed by the method shown in process drawing of [drawing 1](#) using 45wt%MDEA solution as a lean solution is explained. Carbon-dioxide-levels 26vol% of natural gas was supplied to the lower part of the absorption tower 2 under pressure 58 kgG/cm² and 25 ** conditions. In the lower absorption part 3, ** wall type packing etc. are filled up with the absorption

tower 2 so that the gas-liquid contact of the partial regeneration lean solution 21 and the natural gas 1 going up can be carried out efficiently. As for the natural gas 1, in the lower absorption part 3, partial removal of the carbon dioxide levels was made even about 3 vol(s)%. In the top absorption part 4, the natural gas 1 going up carried out gas-liquid contact of the natural gas 1 to the reproduction lean solution 22 efficiently by the same ** wall type packed bed, it became the purified gas 17, and was discharged from the absorption tower crowning. The purified gas 17 was carbon dioxide levels of 50 ppm, the temperature of 50 **, and pressure 58 kg/cm².

[0029]The load lean solution 20 which absorbed carbon dioxide was heated by 130 ** after heat exchange, it was supplied to the high voltage regeneration tower 8, and partial regeneration was carried out. Since the carbon dioxide and the lean solution 20 which were in the free state with said heating in the high voltage regeneration tower 8 are separated and it is considered as the partial regeneration lean solution 21, especially the warmer of reboiler 12 grade is unnecessary, but it may install if needed. It was cooled by the capacitor 9 and the separated carbon dioxide, water, and a little absorbents were separated by the gas liquid separation device 10 from the carbon dioxide 18. The carbon dioxide 18 by which cooling separation was carried out is the almost same high voltage as pressure 55 kg/cm² and the natural gas 1 of a raw material at about 40 **. It is compressed into 150 kg/cm² by the compressor which is not illustrated, and it can be used for the 3rd recovery of a crude oil, or can use for subterranean preservation.

[0030]On the other hand, the partial regeneration lean solution 21 extracted from the bottom of the high voltage regeneration tower 8 is about 130 ** in temperature, and the specified quantity was supplied to the lower absorption part 3 of the absorption tower 2. In the meantime, the 130 ** partial regeneration lean solution 21 carried out heat exchange to the low-temperature load lean solution 20, and was cooled to a still more nearly required temperature. It was supplied to the low-pressure regeneration tower 11, the remainder of the partial regeneration lean solution 21 was decompressed by 0.85 kg/cm², emitted the carbon dioxide 19 and water from the overhead, and was reproduced. The bottom was heated by about 130 ** with the reboiler 12 formed in the lower part of the low-pressure regeneration tower 11, and was recycled by the low-pressure regeneration tower 11, and the reproduction lean solution 22 of abbreviation 45wt%MDEA was obtained. It was cooled by the capacitor 13 and the separated carbon dioxide, water, and a little absorbents were separated by the gas liquid separation device 14 from the carbon dioxide 19. The carbon dioxide 19 by which cooling separation was carried out is pressure 0.35 kg/cm² at about 40 **. It is used as industrial gas.

[0031]The reproduction lean solution 22 extracted from the bottom of the low-pressure regeneration tower 11 is about 130 ** in temperature, and was supplied to the top absorption part 4 of the absorption tower 2. In the meantime, the 130 ** reproduction lean solution 22 carried out heat exchange to the low-temperature load lean solution 20, and was cooled to a still more nearly required temperature. That by which the recovery amounts of carbon dioxide were collected from the high voltage regeneration tower 8 is 85%.

It was 15% which was collected from the low-pressure regeneration tower 11.

Thus, the carbon dioxide in the refining natural gas 17 falls to the concentration which does not generate solid dry ice at the time of LNG manufacture, and since the pressure of the collected carbon dioxide is high, Compression power required to manufacture the liquefied carbonic acid used for the 3rd recovery of a crude oil was saved, and the scale of equipment was also reduced.

[0032](Example 4) The case where it removes by the method shown in process drawing of drawing 1 using the solution which contains the carbon dioxide in the raw material hydrogen gas for composition produced by reforming natural gas as a lean solution, and contains piperazine 4% in 40wt% triethanolamine (TEA) as a reaction accelerator is explained. The material gas 1 containing 68 mol of hydrogen %, methane 12mol%, and 19 mol of carbon dioxide % and other inert gas was supplied to the lower part of the absorption tower 2 at pressure 33 kgG/cm² and the temperature of 60 **.

[0033]In the absorption tower 2, the material gas 1 going up carried out gas-liquid contact to the partial regeneration lean solution 21 in the lower absorption part 3. As for the material gas 1, in the lower absorption part 3, partial removal of the carbon dioxide levels was made even about 1 vol%. In the top absorption part 4, gas-liquid contact of the material gas 1 was carried out to the reproduction lean solution 22, it became the purified gas 17 of carbon dioxide levels of 200 ppm, the temperature of 40 **, and pressure 32 kgG/cm², and was discharged from the absorption tower crowning. The load lean solution 20 which absorbed carbon dioxide was heated by 120 ** after heat exchange, the high voltage regeneration tower 8 was supplied, and about 60% of carbon dioxide in the load lean solution 20 was emitted. It was cooled by the capacitor 9 and the separated carbon dioxide, water, and a little absorbents were separated by the gas liquid separation device 10 from the carbon dioxide 18. At about 40 **, the carbon dioxide 18 by which cooling separation was carried out is pressure 9 kgG/cm², was compressed into 100 kgG/cm² by the compressor which is not illustrated, and was used for liquefied carbon dioxide composition.

[0034]On the other hand, heat exchange was carried out to the load lean solution 20, and it was cooled further, and circulated through the partial regeneration lean solution 21 extracted from the bottom of the high voltage regeneration tower 8 to the lower absorption part 3 of the absorption tower 2. It was supplied to the low-pressure regeneration tower 11, about 10% of the remainder of the partial regeneration lean solution 21 was decompressed by 0.85 kgG/cm², emitted carbon dioxide and water from the overhead, and was reproduced. The bottom was heated by about 130 ** with the reboiler 12 formed in the lower part of the low-pressure regeneration tower 11, and was recycled by the low-pressure regeneration tower 11. Thus, as for the reproduced lean solution 22, about 98% of carbon dioxide was emitted on the basis of the original load lean solution 20. Although the carbon dioxide 19 separated by the gas liquid separation device 14 was pressure 0.35 kgG/cm² at about 40 **, this was also compressed into 100 kgG/cm² by the compressor, and was used for liquefied carbon dioxide composition.

[0035]The reproduction lean solution 22 extracted from the bottom of the low-pressure regeneration tower 11 is about 130 ** in temperature, and is supplied to the top absorption part 4 of the absorption tower 2. In the meantime, heat exchange of the reproduction lean solution 22 was carried out to the low-temperature load lean solution 20, and it was further cooled by cooling water. That by which the recovery amounts of carbon dioxide were collected from the high voltage regeneration tower 8 is 92%.

It was 8% which was collected from the low-pressure regeneration tower 11. Thus, since the ratio of the carbon dioxide which the carbon dioxide in raw material hydrogen gas for composition fell to sufficient concentration to supply a tail end process, and was collected with high voltage was high, compression power required for liquefied carbon dioxide manufacture was saved, and the scale of equipment was also reduced. [0036](Comparative example 1) The high voltage natural gas raw material and absorbent which were used in Example 3 were used, conventionally, by the process (refer to drawing 2), natural gas was decreased in carbon dioxide levels even of 50 ppm, and carbon dioxide was collected further. In the 1st flash drum 123, the flash plate of the carbon dioxide load lean solution 120 is carried out by 3.8 kgG/cm², it separates some carbon dioxide in the load lean solution 120, and is taken as a partial regeneration lean solution. This partial regeneration lean solution was further heated with the warmer 107, and subsequently to the 2nd flash drum 124 was supplied, and the flash plate was carried out again, and it obtained the reproduction lean solution 122. [0037]The pressure of the carbon dioxide obtained with the 1st flash drum 123 is 3.8 kgG/cm².

As compared with pressure 55 kgG/cm² of the carbon dioxide obtained in Example 1, it was substantially low, and disadvantageous to manufacture the liquefied carbonic acid used for the 3rd recovery of a crude oil in respect of compression power and equipment as compared with Example 1.

The natural gas 101 is supplied to the absorption tower 102, and serves as the purified gas 117. The overhead capacitor by which 109 has been arranged between the 2nd flash drum 124 and the separation drum 110, the carbon dioxide in which 118 was emitted from the separation drum 110, the carbon dioxide in which 132 was emitted from the 1st flash drum 123, and 116 are condensators.

[0038]

[Effect of the Invention]It became possible to remove high-pressure natural gas and the high concentration carbon dioxide in various synthesis gas to the minute amount concentration of 1000 ppm or less, and to collect carbon dioxide with high voltage by this invention, and compression power was saved to the post utilization of carbon dioxide, and the scale of equipment was also reduced.

CLAIMS

[Claim(s)]

[Claim 1]High-pressure material gas containing carbon dioxide is supplied to decarbonator which consists of a lower absorption part and a top absorption part, Partial absorption of the carbon dioxide is gas-liquid-contact-carried out by making material gas into a partial regeneration lean solution by a lower absorption part, Discharge purified gas which carried out gas-liquid contact to a reproduction lean solution by a top absorption part, absorbed a small amount of carbon dioxide until it became concentration, and removed this carbon dioxide out of a system, and. Heat a carbon dioxide load lean solution produced in decarbonator, and a high voltage regeneration tower is supplied, After emitting some carbon dioxide under application of pressure and obtaining a partial

regeneration lean solution, this a part of partial regeneration lean solution is supplied to a lower absorption part, Supply the remainder to a low-pressure regeneration tower, and emit carbon dioxide, obtain a reproduction lean solution, and this reproduction lean solution is supplied to a top absorption part, Carry out vapor liquid separation from moisture which cools carbon dioxide emitted under application of pressure, and is accompanied on the other hand in a high voltage regeneration tower, and carbon dioxide under application of pressure is collected, Advanced removal and a high voltage recovery method of carbon dioxide in high voltage material gas carrying out vapor liquid separation from moisture which cools carbon dioxide emitted in a low-pressure regeneration tower, and is accompanied, and collecting carbon dioxide.

[Claim 2]Advanced removal and a high voltage recovery method of carbon dioxide in the high voltage material gas according to claim 1 whose carbon dioxide levels in the above-mentioned high-pressure material gas are 2 to 50%.

[Claim 3]Advanced removal and a high voltage recovery method of carbon dioxide in the high voltage material gas according to claim 1 or 2 whose pressure of the above-mentioned high-pressure material gas is more than 2 kg/cm^2 (absolute pressure).

[Claim 4]Advanced removal and a high voltage recovery method of carbon dioxide in the high voltage material gas according to any one of claims 1 to 3 whose carbon dioxide levels in the above-mentioned purified gas are 10-10000 ppm.

[Claim 5]Advanced removal and a high voltage recovery method of carbon dioxide in the high voltage material gas according to any one of claims 1 to 4 whose cooking temperature of a carbon dioxide load lean solution when emitting some carbon dioxide from the above-mentioned carbon dioxide load lean solution and obtaining a partial regeneration lean solution is 90-150 **.

[Claim 6]Advanced removal and a high voltage recovery method of carbon dioxide in the high voltage material gas according to any one of claims 1 to 5 whose pressures when emitting some carbon dioxide from the above-mentioned carbon dioxide load lean solution and obtaining a partial regeneration lean solution are 2 kg/cm^2 (absolute pressure) - a feed gas pressure.

[Claim 7]Advanced removal and a high voltage recovery method of carbon dioxide in the high voltage material gas according to any one of claims 1 to 6 whose cooking temperature of a partial regeneration lean solution when emitting carbon dioxide from the remainder of the above-mentioned partial regeneration lean solution and obtaining a reproduction lean solution is 100-150 **.

[Claim 8]Advanced removal and a high voltage recovery method of carbon dioxide in the high voltage material gas according to any one of claims 1 to 7 whose pressure when emitting carbon dioxide from the remainder of the above-mentioned partial regeneration lean solution and obtaining a reproduction lean solution is less than 2 kg/cm^2 (absolute pressure).

[Claim 9]High-pressure material gas characterized by comprising the following is supplied to decarbonator, Discharge purified gas which gas-liquid-contact-carried out partial absorption of the carbon dioxide by making material gas into a partial regeneration lean solution by a lower absorption part, carried out gas-liquid contact to a reproduction lean solution by a top absorption part, absorbed a small amount of carbon dioxide to concentration, and removed this carbon dioxide out of a system, and. Heat a carbon dioxide load lean solution produced in decarbonator, and a high voltage regeneration

tower is supplied, After emitting some carbon dioxide under application of pressure and obtaining a partial regeneration lean solution, a part of partial regeneration lean solution is supplied to a lower absorption part, Supply the remainder to a low-pressure regeneration tower, emit carbon dioxide, and a reproduction lean solution is obtained, Supply a reproduction lean solution to a top absorption part, carry out vapor liquid separation from moisture which cools carbon dioxide emitted under application of pressure in a high voltage regeneration tower by a condensator and a gas liquid separation device in which it was provided by high voltage regeneration tower crowning, and is accompanied, and it collects carbon dioxide under application of pressure, Advanced removal and a high voltage recovery system of carbon dioxide in high voltage material gas carrying out vapor liquid separation from moisture which cools carbon dioxide emitted in a low-pressure regeneration tower by a condensator and a gas liquid separation device in which it was provided by low-pressure regeneration tower crowning, and is accompanied, and collecting carbon dioxide.

Decarbonator which consists of a lower absorption part and a top absorption part.

A warmer of a carbon dioxide load lean solution.

A high voltage regeneration tower of a carbon dioxide load lean solution.

A condensator and a gas liquid separation device which were provided in a high voltage regeneration tower crowning, a low-pressure regeneration tower of a partial regeneration lean solution, a warmer of a low-pressure reproduction bottom, and a condensator and a gas liquid separation device that were provided in a low-pressure regeneration tower crowning are comprised, and it is carbon dioxide.